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Aluminum Acetate in the Development of Alum Retannage*

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We have previously reported [1,2,3,4] that alum retannage imparts to vegetable-tanned leathers resistance to deterioration such as that caused by acids (which may be absorbed from acid-polluted atmospheres), moist heat, or molds. These reports show some of the chemical and physical changes which occur in vegetable-tanned leather when treated by this process. The amount of combined tannin is increased, with a corresponding decrease in the amount of soluble tannin. There is an increase in the degree of tannage. There is

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a rise in the shrinkage temperature to more than 100°C. Tensile strength, stretch, and water vapor permeability are only slightly affected by the retannage. Porosity is increased, and water absorption is somewhat decreased. Like leather tanned by other types of mineral tannage, alum-retanned leather is difficult to "wet back" after it has been completely dried. (These changes are shown by the data from one of these reports [1], given in Table I.) These properties suggested that alum retannage might be advantageously used to overcome insole failures, which are a serious problem in Army shoes. Preliminary track and actual wear tests indicated that replacement of vegetable-tanned leather insoles by alum-retanned leather insoles would materially reduce the number of failures.

TABLE I

Effect of Alum Retannage on Vegetable-Tanned Leather

	Vegetable-Tanned Leather	Alum-Retanned Leather
Al_2O_3, per cent	——	2.8
Soluble tannin, per cent	12.2	7.5
Combined tannin, per cent	35.2	39.9
Degree of tannage, per cent	76	90
Shrinkage temperature, degrees cent.	87	112
Tensile strength, lbs./sq. inch	1900	2020
Relative porosity	151	334
Relative water vapor permeability	0.5	0.6
Stretch at breaking point, per cent	22	30
Water absorption, per cent	52	44

The method of retannage, as previously reported, called for a comparatively weak liquor consisting of an aqueous solution of aluminum sulfate made to a basicity of 25° Schorlemmer and containing one mole of sodium acetate for each mole of Al_2O_3 as a "masking" or stabilizing agent. Tanning with this liquor in tanning vats or drums required several days. Later work has been directed toward developing a more rapid process, which could be easily and effectively applied in a commercial tannery to supply sufficient leather for a wear test on a fairly large scale.

With this objective, attempts were made to develop a "dry-dip" method. In this method, the dry leather is dipped into an alum solution of the proper strength and temperature. When the leather has absorbed a sufficient amount of the solution, it is removed, sammied and dried. During sammying and drying, the absorbed Al_2O_3 combines with the leather. The dip solution used was a solution of aluminum sulfate made to 25° basicity with sodium carbonate and containing sodium acetate. In these preliminary dry-dipping tests, penetration was poor, combination of Al_2O_3 with the leather was incomplete, and the mineral content of the leather was high. Apparently the dry-dipping process was unsatisfactory when aluminum sulfate and sodium acetate solutions were used.

Another method studied was the incorporation of the aluminum salts in the conventional tanner's oil wheel with the oil and other ingredients commonly added to the leather in this manner. Table II shows results of several pilot-scale tests of this method.

TABLE II

Pilot-Scale Oil Wheel Retannage Tests with Aluminum Sulfate*

Test Number		1	2	3	4
Aluminum sulfate $Al_2(SO_4)_3 18H_2O$, used,	pounds	16.0	24.0	32.0	55.0
Sodium acetate $NaAc.3H_2O$ used,	pounds	3.2	4.8	6.4	11.0
Alkali used,	pounds	2.6**	4.0**	6.7**	9.1†
Borax used,	pounds	1.2	1.8	2.4	4
Epsom salts added,	pounds	5.3	5.3	5.3	7
Other materials added††	pounds	8.2	8.2	8.2	7
Total ash in leather,	per cent	11.2	15.9	17.5	17.9
Combined Al_2O_3 in leather,	per cent	1.8	2.8	3.2	4.9
Shrinkage temperature of leather,	°C.	92–95	98–105	105–107	102–108
pH of leather,		3.59	3.90	4.01	3.87

*Retanning materials were dissolved to a concentrated solution before they were added to the oil wheel. Twenty-five bellies, equivalent to approximately 125 lbs. of dry leather, were used in each test.

**Sodium hydroxide.

†Sodium carbonate.

††This includes all materials normally added in the oil wheel except oil and epsom salts. The leathers received the regular oil mix.

For each of these tests, 25 bellies, totaling approximately 125 pounds dry weight, were used. The amounts of aluminum sulfate, sodium acetate, and borax used were varied as shown in Table II. The wet bellies, after bleaching and wringing at the tannery, were taken to the laboratory and put in the warmed laboratory oil wheel (inside size, 30″ wide x 6′ diameter). The retanning solution, containing aluminum sulfate, sodium acetate and alkali, and the sugar and oils at 155° F., were added while the wheel was running. In Test No. 4, borax and Epsom salts were added in the tanning liquor; in the other tests, the salts and filler materials were added dry before starting the wheel. The stock was drummed for 1 hour, after which the leather was removed, allowed to sammy, and dried slowly for 8 days. The leathers from Tests 1, 2, and 3 were rough dried at the tannery, that from Test 4 was dried at the laboratory. After rough drying, all the leathers were sour-dipped, rolled, and dried at the tannery.

The results in Table II show that with increasing amounts of aluminum sulfate used there was a corresponding increase in the combined Al_2O_3 in the leather (the average values obtained from a representative number of bellies). The percentage of Al_2O_3 varied slightly from belly to belly in the same lot, as indicated by the range in shrinkage temperatures. When finished and dried at the laboratory, the bellies had little tendency toward cracky grain. When they were finished, rolled, and dried at the tannery, however, the grain was cracky. The difference in drying technique between the laboratory and the tannery was that in the laboratory the leathers were slowly dried until they reached the proper moisture condition, whereas in the tannery they were dried beyond this point and then wet back to give the desired moisture content.

This retanning process was then applied on a tannery scale; 200 bellies were used for each of four tests. Various amounts of materials were used, as indicated in Table III. After bleaching and wringing as usual, 200 bellies were placed in the oil wheel. For tests 1 and 2, salts, filler, borax, and clay were added dry, and the wheel was run for 3 minutes; then the alum retannage solution was added, and the wheel was run for 40 minutes. Next, the oil-sugar mixture was added, and the wheel was run for 20 minutes. In Tests 3 and 4 the aluminum sulfate, sodium acetate, and borax were added separately in dry form in the order given, and the wheel was run for 15 minutes after each addition. The regular filler materials and salts were then added, and the wheel was run for 5 minutes. The liquid sugar-oil mix was next pumped into the wheel and the wheel was run for 10 minutes.

TABLE III

Plant-Scale Oil Wheel Retannage Tests with Aluminum Sulfate*

Test number		1**	2†	3†	4†
Aluminum sulfate, used,	pounds	400	100	100	150
Sodium acetate, used,	pounds	50	12	12	18
Alkali used,	pounds	65††	10‡	——	——
Borax used,	pounds	30	8	50	75
Epsom salts added	pounds	32	32	32	20
Other materials added‡‡	pounds	140	140	140	140
Total ash in leather,	per cent	20.5	10.0	11.9	13.4
Combined Al_2O_3 in leather,	per cent	5.7	1.6	2.1	2.9
Shrinkage temperature of leather,	°C.	101–108	83–85	88–89	93
pH of leather,		3.82	3.29	3.49	3.51

*Two hundred bellies, equivalent to approximately 1,000 lbs. of dry leather, were used for each test.
**All retanning materials dissolved to a conentrated solution before adding to the oil wheel.
†All materials added dry to the oil wheel.
††Sodium carbonate.
‡Sodium hydroxide.
‡‡This includes all material normally added in the oil wheel except oil and epsom salts. The leathers received the regular oil mix.

Table III shows the results of these tests. In the first test, a much higher fixation of alum was obtained than desired, because the amounts of materials used were calculated on an average 5-pound belly, whereas actually the bellies weighed far less. The bellies from this first test were quite cracky. Bellies from Tests 2 and 3 showed practically no crackiness; those from Test 4 showed slight crackiness. These results indicated that from 2.50 to 2.75 per cent Al_2O_3 would probably be the optimum amount. Comparison of Tables II and III shows that the shrinkage temperatures in Table III were not so high as would be expected from the Al_2O_3 content. This may have been due to poor combination of the Al_2O_3 when added dry. In addition, when the materials were added dry there was a wide variation of Al_2O_3 content in bellies from the same lot, thus indicating uneven distribution.

As shown by Tables II and III, the ash content of the leathers retanned in the oil wheel was high. It was much higher than that obtained in our previous method of tannage. This may be explained by the difference in the methods used. In vat or drum retanning with a comparatively weak alum liquor, the Al_2O_3 is thoroughly combined, and is not removed by subsequent washing. The remaining mineral matter in the liquors is not combined, and is quite thoroughly removed by washing. In the oil-wheel process, however, none of the uncombined mineral matter is removed because there is no subsequent washing, and therefore it remains in the leather and increases the ash content. It was believed that this high mineral content might be one cause of crackiness; therefore it seemed advisable to obtain a retanning solution containing less mineral matter.

It seemed possible that this mixture of aluminum, sulfate, sodium, and acetate ions might be replaced by a mixture of aluminum and acetate ions, which would be given by aluminum acetate. The stabilizing acetate ion would be given directly by the salt used, and, in addition, less alkali would be required to bring the solution to the desired pH. A solution of aluminum acetate may easily be prepared, but the preparation of a powder or even a concentrated solution presents some difficulties.

An aluminum acetate solution of satisfactory purity was prepared in the laboratory by the reaction between solutions of aluminum sulfate and calcium acetate; the precipitated calcium sulfate was filtered off. Since this solution was too dilute to use by the oil-wheel method, tests were made by the dry-dip process previously found unsatisfactory for the aluminum sulfate-sodium acetate method. In preliminary laboratory tests with the aluminum acetate solutions, results were quite satisfactory. It was found that the distribution, penetration, and combination of the Al_2O_3 were good. These results indicated that a dry-dip process might be satisfactory if an aluminum acetate solution were used instead of an aluminum sulfate-sodium acetate solution.

As a quick means of determining the amount of combination and the distribution of the Al_2O_3 in the leather, we have found shrinkage temperature determinations and a simple boiling test very valuable. Although it is not necessarily true for all leathers that quality may be judged by resistance to moist heat, much information in regard to the completeness and uniformity of retannage in the alum-retanned leathers may be obtained by these tests. If, after being exposed for 3 minutes to boiling water, the leather does not shrink or shrivel and darken in the interior it may be judged that combination and distribution of the Al_2O_3 are satisfactory.

It might not be feasible to prepare an aluminum acetate tanning solution in the tannery by the reaction between aluminum sulfate and calcium acetate. However, manufacturers of aluminum compounds have now developed a method of preparing an easily soluble basic aluminum acetate powder. Solutions of this material containing the equivalent of 3 to 5 per cent Al_2O_3 have pH values of 4.4 to 4.8, well within the optimum range for fixation of Al_2O_3 in leather. Laboratory tests indicated that this material was quite satisfactory for retannage.

Retannage tests were made with basic aluminum acetate for producing alum retanned leathers in both pilot-scale and plant-scale lots. Results of these tests have been summarized in Table IV. The first was a pilot-scale test conducted in the laboratory in which 21 bellies were used. The aluminum acetate in concentrated solution was applied uniformly to the bellies by hand; they were then put in the laboratory oil wheel and drummed with the regular tannery filler materials for 10 minutes. The regular tannery sugar-oil mixture was added to the running wheel, and the wheel was run for 55 minutes. The bellies were then removed, piled and allowed to sammy for 48 hours, after which they were returned to the tannery for drying and finishing.

TABLE IV

Oil Wheel Retannage Tests with Aluminum Acetate

		Pilot Scale (Laboratory)	Plant Scale (Tannery)	
Estimated weight of bellies	pounds	105	1,000	1,000
Aluminum acetate used	pounds	11.7*	106*	50**
Epsom salts used	pounds	3.0	0	16
Ash in leather	per cent	9.9	8.4	2.6–3.5
Al_2O_3 in leather	per cent	4.6	3.5	1.4–2.1
Shrinkage temperature	°C.	116	116	91–104
pH of leather		3.90	4.43	3.70–3.89

*Aluminum acetate added in solution.
**Aluminum acetate added dry.

The other two tests were made on a plant-scale at the tannery. In the first of these tests, 200 bleached and wrung bellies were placed in the oil wheel, the concentrated solution of aluminum acetate was poured in, and the wheel was run for 20 minutes. The regular quantity of filler, but no Epsom salts, was added, and the wheel was run for 10 minutes, after which the regular sugar-oil mix was pumped in, and the wheel was run for 30 minutes. The leather was then slowly dried, sour-dipped, rolled, and finished. In the second test, the bellies were washed with water in a wheel, then bleached and wrung before the alum retannage was applied. The amounts of aluminum acetate and Epsom salts were 50 pounds and 16 pounds, respectively. These materials were added in dry form, and the wheel was run for 10 minutes. The usual sugar-oil mixture and clay were added, and the wheel was run for 10 minutes. No fillers were used. The bellies were slowly dried, sour-dipped, rolled, and finished.

In the pilot-scale test and the first tannery test, the aluminum acetate was dissolved before it was added. In the other test, the dry material was added, and the results show that there was considerable variation in the completeness of retannage between the individual bellies in this test. It is believed that application of aluminum acetate in dry form results in nonuniform absorption and retannage. The results obtained in these tests, however, indicate that the use of aluminum acetate instead of the aluminum sulfate-sodium acetate mixture gives a firmer combination of Al_2O_3, as the shrinkage temperatures in general are higher for a comparable amount of total Al_2O_3. The amount of mineral matter is also reduced. All these leathers, when dried slowly in the laboratory to the proper moisture content, showed little tendency toward cracky grain. When they were overdried, however, and then wet back, the grain became tender. Figure I shows the stratigraphic distribution of Al_2O_3 in the leather when this method was used.

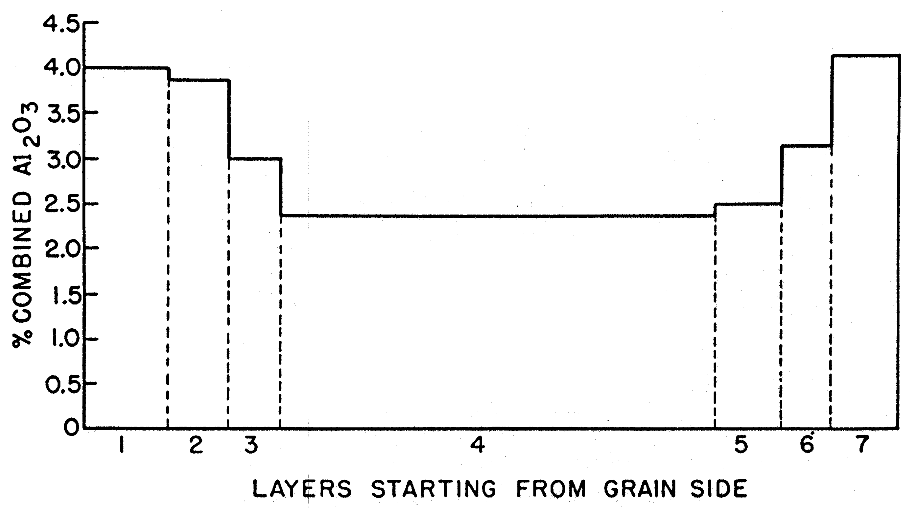

FIGURE 1. Stratigraphic Distribution of Al_2O_3 in Leather. Aluminum Acetate-Oil Wheel Method.

Commercial basic aluminum acetate was also used successfully in dry dipping tests. Table V shows some of the conditions studied, and the results obtained by dipping at 45° C., which appeared to be the optimum temperature. Concentration of solution and time of dipping were varied. The results indicated that a dipping time of ½ hour will usually be satisfactory. The concentration of the solution must be varied according to conditions. Leathers from different tannages vary in the amount of solution they will absorb in a given time, and this point must be determined by test. Furthermore, leathers of different thickness from the same tannage will have different absorption capacities, so leathers must be sorted into three or four thickness classifications before dipping. The variations in pickup of solution and Al_2O_3 shown in Table V are wide, but represent various tannages. The last five tests, which were made with leather of the same tannage, show the variations, due mostly to thickness, which might be expected. The data show that, under proper conditions, leather of the desired Al_2O_3 content, probably 2.50 to 2.75 per cent, may be made and that the Al_2O_3 in this leather will be firmly fixed and well distributed, as indicated by boiling tests and shrinkage temperature determinations.

TABLE V

Dry-Dip Retannage Tests with Aluminum Acetate at 45° C.

Test number	1	2	3	4	5	6	7	8	9	10
Concentration of solution in Al_2O_3, per cent	2.5	3.0	3.0	3.0	4.0	4.0	4.0	4.6	5.3	5.3
pH of solutions	——	4.42	——	4.47	——	——	——	4.49	——	4.55
Time of dipping, minutes	10	5	10	60	10	30	30	30	30	30
Pickup of solution on dry leather weight, per cent	66.7	63.3	84.4	58.8	101.7	36.8	50.0	51.0	54.7	57.0
Ash in leather, per cent	3.1	5.1	5.6	4.3	5.2	3.2	5.5	5.2	5.5	6.6
Al_2O_3 in leather, per cent	1.8	2.5	3.1	2.0	3.0	1.9	2.5	2.6	3.0	3.3
Shrinkage temperature of leather, °C.	100	109	115	100	124	102	110	111	116	116

A number of insoles were retanned in the laboratory for testing by the Office of the Quartermaster General of the Army. In carrying out the retannage of these insoles, several results were observed that indicated that the retannage process could be applied more advantageously to bellies or belly centers than to finished cut soles. In the first place, the finished cut soles contain a fairly large amount of loading material and have been rolled and finished to the desired degree of firmness. Retannage of finished cut soles tends to increase to an undesirable extent both the mineral matter content and the firmness of the leather. The edges of the soles became overtanned and cracky. Insoles are cut from leather which has been rolled in a moist condition. Some of the leather fibers have been put under an unnatural tension, which is released when the leather is wet. During the wetting operations incidental to alum retannage, this tension is released, resulting in a distortion of the sole pattern. For these reasons, we have found it desirable to apply the alum retannage to rough bellies and then load and finish to the required firmness. This procedure will reduce the losses resulting from shrinkage, distortion, and edge effect to a minimum.

One objection to alum retannage is the production of tender or cracky grain. For many purposes where the grain is to be removed by light buffing, this is of little significance. We have found that crackiness may be largely eliminated by observing certain precautions. The amount of Al_2O_3 in the leather should be no higher than necessary. A desirable range appears to be 2.5 to 2.75 per cent. The amount of other mineral matter, such as Epsom salts, added to the leather should be reduced so that the total mineral matter will not be excessive. A light oiling of the leather after retannage is beneficial. Finally, the leather should not be overdried, which appraently is one cause of crackiness.

Summary

The use of basic aluminum acetate for alum retannage of vegetable-tanned insole leather was shown to be more effective than retannage with aluminum sulfate which has been stabilized and neutralized to the desired basicity. Retannage may be carried out in regular tannery oil drums, but results indicate that retannage applied in the form of a dry dip to rough whole bellies or belly centers followed by oiling and finishing is to be preferred. In applying the retannage, the tanner will find it necessary to adjust the process to his own type of leather.

For the appraisal of serviceability, leather should be produced commercially by the proposed method in quantity adequate for large-scale wear tests.

References

1. Beebe, C. W., and Frey, R. W., *J. Am. Leather Chemists' Assoc.*, **37**, 478 (1942).
2. Beebe, C. W., and Frey, R. W., *ibid.*, **37**, 539 (1942).
3. Beebe, C. W., Rogers, J. S., and Happich, W. F., *ibid.*, **44**, 204 (1949).
4. Frey, R. W., and Beebe, C. W., *ibid.*, **35**, 440 (1940).

Discussion

S. S. Kremen: Those of you who have followed the work with the improvement of insole leather know that the alum retannage is considered to be fundamentally capable of marked improvement.

The principal weakness which has to be overcome is the cracky grain or tender fiber. Certainly Mr. Beebe has indicated that the possibility is that it can be done.

I believe from talking to Mr. Rogers that there is one fundamental problem which is causing most of this trouble—a problem which is common to all attempts to retan or post-tan vegetable leather as produced in the tannery.

You have to clean the grain and bleach it in the tannery. You could just follow the bleach, but at that stage the stock is coming through quite rapidly, and it is moved to the wringer in large amounts. You cannot then, without causing quite a bit of disruption in the tannery process, leave the stock overnight in the tanning bath in the optimum way.

In this whole business you can have a great deal of trouble in any retanning with formaldehyde and chrome as well as the alum if you try to do it without assuring slow and uniform penetration and going through a thorough stripping to protect yourself from this cracky grain.

The whole problem is, that if you want some improvement in the quality of your leather, you have to be prepared to make some modifications in the process along the lines that Dr. Merrill pointed out. Yes, it is surprising when you make an improvement if you don't have to rebalance your whole process.

I think all of us who are trying to improve the quality of insole leather are meeting with that very problem—this understandable hesitancy to rebalance the whole procedure while keeping it on an economic basis so that you can do your post-tanning.

What I feel is the key to all these troubles that you run into is that there must be recognition that the whole process should be considered. It might possibly be the case that retannage may be done more conveniently at a different stage. Most of them now are done either in the oil wheel or dip.

I wonder if anybody has any idea whether perhaps you might get sufficient improvement without the undesirable properties by doing it after the rocker yard when you may have sufficient tannage, and also the time to conveniently handle the procedure.

Beebe: I think it would be most desirable to adjust the retannage to fit a normal tanning process as nearly as possible.

Kremen: Are there any questions or comments from the floor?

J. S. Rogers: In our early studies of alum retannage, we did use some leather taken at earlier stages in the tanning, and that worked quite satisfactorily.

Later on we thought it desirable to consider doing this work after the bleach because we found that bleaching leather after it had been alum retanned had a tendency to remove the alum tannage from the surfaces of the leather, particularly the grain surface, and some from the flesh surface. Such leathers, when subjected to the boil test would show a certain amount of shrinkage in these areas after bleaching.

That is one of the reasons why we thought it desirable to do this work after bleaching. I think the alum retannage applied to leathers that have been partially stripped to remove excessive tanning materials from the grain area is desirable because the application of the alum retannage in the grain results, as you probably have noticed, in a fixation of any uncombined tanning materials that are there. That, naturally would have a tendency to form an area that would be likely to be brittle and have a tendency to crack.

We feel that this difficulty can be overcome. In fact, we have prepared samples in the laboratory that have been successful in this direction, and we believe further tests in the tannery will enable us to prepare a leather that will be satisfactory in that respect.

We have developed in the laboratory a testing machine which is ready for making dynamic tests on the insole leathers when we have leather that we feel will justify actual testing in this way, and also have a sufficient quantity of leather for use in actual service tests for correlation with the laboratory tests.

I think then we will be able to appraise these leathers more satisfactorily.

Kremen: I would like to know the preferred pH range for alum retannage. Secondly, was any work done on a companion or comparatively similar process based on aluminum formate.

C. W. Beebe: The pH range runs 3.8 to 4. In regards to the use of aluminum formate there was none commercially available.

Furthermore, we have tried sodium formate in our previous tests along with other materials, and found sodium acetate was the best stabilizing material for alum retannage. That doesn't necessarily apply to chrome retannage but does to alum.

If there is a commercial aluminum formate available we would like to try it.